



Photopolymerization of Pollen Based Biosourced Composites and Applications in 3D and 4D Printing

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Pollen have the potential to be effective plant-based biorenewable reinforcing fillers for polymers due to their chemical stability and unique micro- or nano-structured surfaces. Pollen-polymer composites can form the basis for a new class of light-weight and sustainable materials if compatible polymer-filler systems can be engineered through photopolymerization, but this idea is previously unexplored. The first demonstration of photopolymerization and 3D printing with the incorporation of pine pollen as filler in poly(ethylene glycol) diacrylate are presented. The filler properties affecting the related depth of cure and the mechanical, thermal, and functional properties are examined in detail. In addition, the lithography technique is applied to the photocomposites for the production of 3D patterns. 4D printing behavior is also possible through the water swelling and dehydration induced actuation of the 3D printed composites with spatial resolution features. This work is expected to provide a new way to a field for photopolymerization reactions in natural material-resin composites and thereby to expand potential applications in 3D and 4D printing.

large quantities from sustainable plant resources.^[14] Pollen has the potential to be an effective bio-filler due to the high strength, chemical stability, low density, and unique architecture of its outer shell.^[15] Biological particles such pollen grains, bacteria, and viruses, have attracted research interest as templates for fabricating inorganic mimics that preserve their unique surface architectures.^[16–19] In particular, pollen grains are thought to be ideal bio-templates for mechanically tough outer shells, highly resistant to heat, chemicals, and oxidation. In addition, pollen exine has been proposed as vehicles for the delivery of pharmaceuticals and vaccines.^[20,21]

Some studies were carried on pollen, while only few studies have reported utilization of pollen as a filler to prepare composites in the field of polymerization. As reinforcing filler, pollen was used in the ther-

moplastics polystyrene,^[15] poly(ϵ -caprolactone),^[15] poly(vinyl acetate),^[22] epoxy,^[18] and trimethylolpropane trimethacrylate,^[23] and poly(ethylene glycol) diacrylate (PEGDA).^[24] To date, the effectiveness of pollen fillers in photopolymerization has remained unexplored and the application of pollen employed as a filler are barely reported in photopolymerization. Therefore, it is quite meaningful to study the photopolymerization of pollen polymer composite.

Commonly, composites are fabricated in photopolymerization, comprising by photoinitiating system (PIS), polymerizable medium (M) and light source (S).^[25,26] Therefore, the design of PIS/M/S systems is a highly attractive and interesting topic, particular for mild conditions (near UV or visible light, rather low-intensity sources, and under air), which drive the photopolymerization of monomer/oligomer formulation with desired properties.^[27–29] Compared to classical polymerization approaches, that is, thermal or redox polymerization, there are numerous advantages for photopolymerization such as high conversion, mild reaction temperature, fast and efficient processes, absence of additional volatile organic compounds including unreacted monomers and fragmentation products, low energy consumption, excellent spatial, and temporal control.^[25,26]

In this work, we demonstrate for the first time the successful incorporation of pine pollen (PP) in PEGDA matrices. The effectiveness of pollen as a reinforcing and strengthening filler in PEGDA is characterized by mechanical properties, interfacial morphology of pollen-polymer composites as a function of pollen loading. Then 3D printing was carried out through laser

1. Introduction

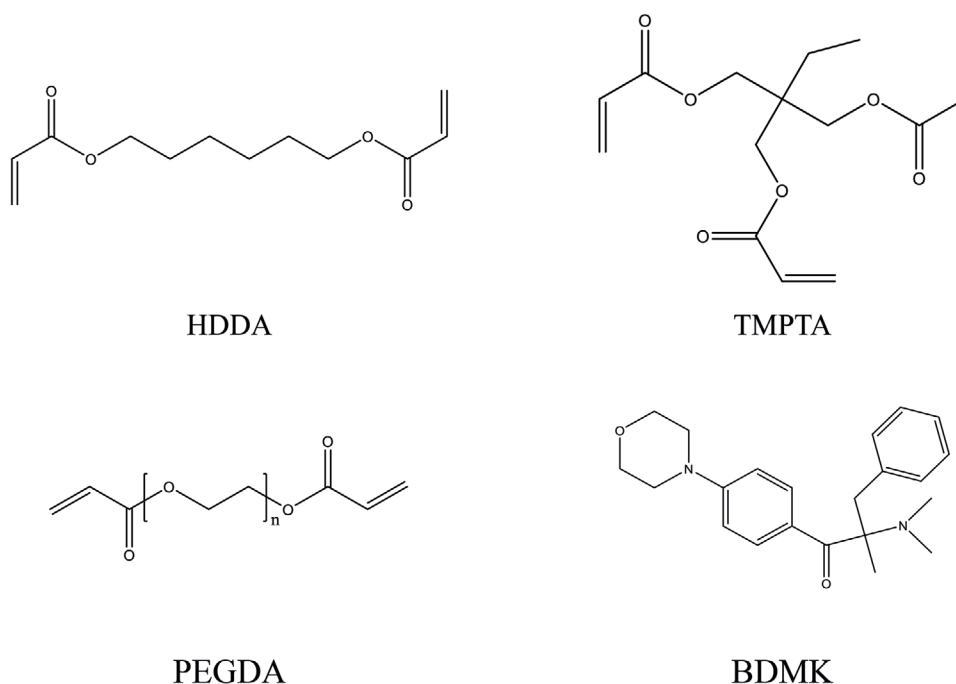
Fillers are often combined with polymers in order to improve their mechanical, thermal, and many other functional properties.^[1–4] Filler materials for property reinforcement in polymer composites range from inorganic ceramics,^[5,6] fibers,^[7,8] micro particles,^[9,10] and zeolites,^[11–13] and many others. However, the use of filler increases the mass of the final parts, because many types of fillers are denser than the matrix polymer. In addition, many mined inorganic fillers are not produced sustainably. Due to increased emphasis on sustainability, there is strong interest in lower-density and sustainably sourced fillers.

Pollen is a ubiquitous natural material which has been sold as a product for medical purposes and can be acquired for

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Scheme 1. Chemical structures of monomers and photoinitiator.

write to form some patterns and water swelling of these 3D patterns were presented. Finally, the material is applied in the field of 4D printing by changing water and temperature factors.

2. Experimental Section

2.1. Materials

The photopolymerizable monomers (trimethylolpropane triacrylate (TMPTA), 1,6-hexanediol diacrylate (HDDA)), the photoinitiator 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (BDMK), and solvent (acetone) were purchased from Allex or Sigma Aldrich and used as received, and their corresponding molecular structures are shown in **Scheme 1**. PEGDA (the average molecular weight was 726 g mol^{-1}) was obtained from Sartomer Europe (SR610) (**Scheme 1**). The PP used as fillers was bought from Blu Damond UGhb (Stuttgart, Germany) without previous treatment and were not washed or treated with organic solvents.

2.2. Pollen-Resin Composite Preparation

The photoinitiators, the photopolymerizable monomers and PP were successively added into a vial, and then a Speedmixer (DAC 150.1 FVZ-K) was used for the mixing with rotation speed at the range of 2000–2500 rpm to produce homogeneously dispersed filled resins which were stored in the dark before photopolymerization reactions. The experimental setup and the basic formulation for the filler-containing composites are illustrated in Figure S1 and Table S1, Supporting Information. Here, the weight percent of the photoinitiator was kept at 1 wt%, and

different kinds of monomers served as benchmark monomers for radical photopolymerization. To study the effect of filler content variation on the photopolymerization kinetics of different monomers, four different filler-contents for composites were elaborately selected, that is, 5, 10, 15, and 20 wt% (values calculated taking into account only filler and monomer).

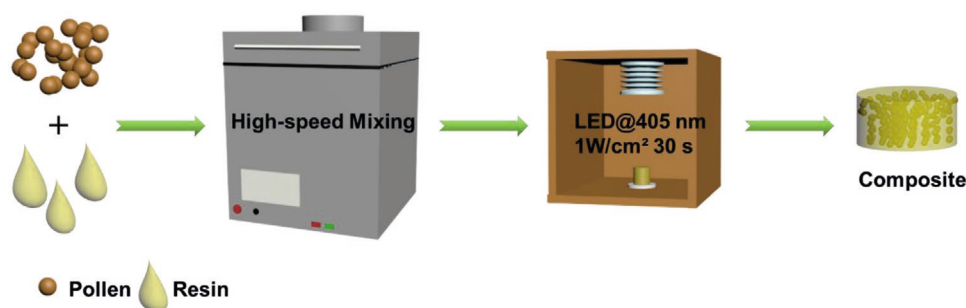
In a LED-curing box, a mold filled with the investigated resin was placed vertically under the light (LED@405 nm; 1 W cm^{-2}) (**Scheme 2**). Then, the sample in the mold was taken out and cleaned by acetone to remove unreacted monomers and uncross-linked pollen until the solution was clear. The polymerized part on the top was employed to measure the depth of cure (DOC) with an Absolute LCD Digimatic Indicator (Mitutoyo).

2.3. 3D Patterns Preparation

A computer-controlled and programmed laser diode (Thorlabs @405 nm, $110 \text{ mW} \cdot \text{cm}^{-2}$) with spot size around $50 \mu\text{m}$ was used for spatial controlled irradiation to produce specific 3D patterns from the photocomposites, which were deposited onto homemade resin tank (2 mm thickness). After the processes of direct laser write (DLW), these 3D patterns were washed with acetone to remove the unreacted monomer. Finally, the printed 3D patterns were observed through a numerical optical microscope (DSX-HRSU, OLYMPUS Corp).

2.4. Material Characterization

The pollen particles sizes and morphology and their corresponding composites were investigated using a JEOL JSM-7900F scanning electron microscope (SEM). The images were acquired



Scheme 2. The preparation process for pollen based composite materials.

at a working distance close to 10 mm and a low accelerating voltage of 2 kV. Prior to these SEM observations, all samples were coated with carbon. Composites were cut with a box cutter.

Thermogravimetric analyses (TGA) were carried out using a METTLER-TOLEDO TGA/DSC 3+ thermoanalyzer. 30 mg samples were heated from 30 to 500 °C at a scan rate of 10° min⁻¹ under nitrogen atmosphere (purge of 100 mL min⁻¹ of N₂ protection gas).

For dynamic thermomechanical analysis (DMA), composites were polished to obtain a pellet with a thickness of 1 mm, and then experiments were performed on a Viscoanalyser METTLER DMA861 at a frequency of 1.00 Hz.

Controlled humidity experiments were performed with humidity chamber Memmert HCP 108.

Samples of composites for water swelling property characterization were prepared in DLW experiments (see Section 2.3), then water swelling property studies were performed. The samples were submerged in distilled water at room temperatures (24 h, 25 °C). The samples were taken out periodically and weighed immediately, after wiping out the water on the surface of the sample, using a precise four-digit balance to find out the content of water absorbed. The measurements were conducted over an equal time period, until a stable sample mass value was obtained. The percentage of water swelling property was calculated by the Equation (1):

$$X = \frac{m_2 - m_1}{m_1} \times 100\% \quad (1)$$

where m_2 is the weight of the sample after 24 h and m_1 is the weight of the dried sample.

3. Results and Discussion

The specific format of a composite-polymer name is monomer-PP@filler content, for example, PEGDA-PP@5% means that the composite is generated from the polymerization of PEGDA with PP as filler and the content of PP is 5 wt%.

3.1. Depth of Cure

The DOC is an important property of light-cured composites, which is defined here as the depth of materials cured adequately under light irradiation @405 nm. In **Figure 1**, the DOC values were obtained, which showed the differences in the DOC values according to the type of monomer and irradiation time. Generally speaking, with the increase of the PP content, the DOC values gradually decreased and even led to very poor photopolymerization in depth, which made the DOC value unmeasurable, that is, the composites cannot be extracted for solvent washing. The increase of PP content is associated with poorer light penetration (i.e., more important light scattering and/or absorption by PP content) leading to lower DOCs.

First, photopolymerization was carried out with different types of monomers (**Figure 1a**). When PP was mixed with

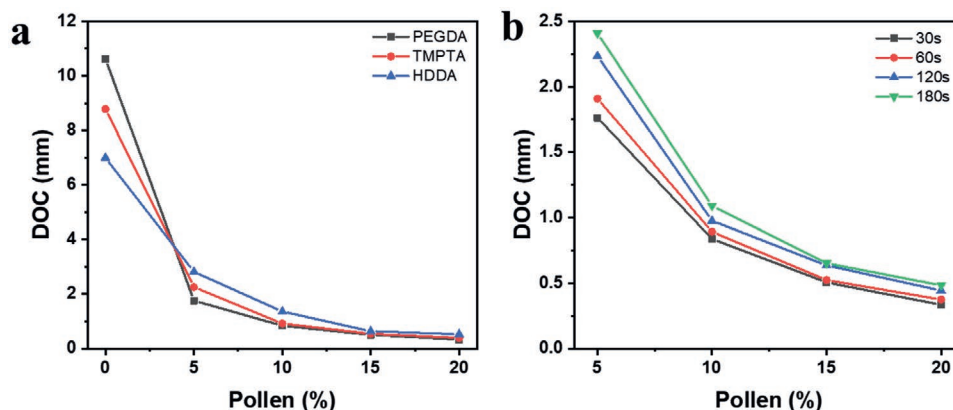


Figure 1. DOC for different factors of the polymerization reaction: a) 3 types of monomers with pine pollen and 1 wt% BDMK; b) different irradiation times for PEGDA with pine pollen and 1 wt% BDMK.

HDDA, the DOC value was much higher than in other monomers at the same PP content. However, in HDDA system, bubbles appeared on the surface of composites (see Figure S2, Supporting Information). Their presence could be related to the air trapped in PP aggregates before mixing. The similar situation occurred in TMPTA system. For PEGDA, although the DOC value was not as excellent as the two mentioned above, the surface of the composite was flat without any bubbles. Remarkably, a good dispersion of pollen is also found in PEGDA based composites after photopolymerization (see SEM below). In addition, the exotherm magnitude of PEGDA-based mixture in the polymerization process was much less obvious than that of HDDA or TMPTA, which may also be a cause of the presence of bubbles in the final composites.

Subsequently, polymerization was carried out with different irradiation times for the PEGDA based systems (Figure 1b). It is obvious to see that with the increase of the irradiation time, the DOC values gradually increased. This suggested that the presence of pollen can affect the light penetration, but the increase of the irradiation time can also effectively increase the DOC value.

3.2. Interfacial Morphology

All the composites and pure pollen powders were observed using SEM. The main morphological characteristics of PPs are shown in Figure 2. The PP is composed of one main part and two airbags, and the diameter is about 50 μm . The SEM images for composites with different filler contents (5%, 10%, 15%,

and 20%) are presented in Figures 3,4 and Figures S3,S4, Supporting Information. Figure 3 shows intimate contact between the pollen and the PEGDA matrix in general with a rather good dispersion on the faces as shown in Figures 3a,b and 4a,b as well as along the cross-section (Figures 3e and 4e). However, many interfacial voids can be found in the surface of composites. With the increase of the pollen content, more and more voids and interphase can be observed. Compared to PEGDA-PP@5%, pollen covered the surface of the composite (PEGDA-PP@20%) almost completely (see in Figure 4). Moreover, the irradiated face (top face) seems to be always flatter than the bottom one.

3.3. Dynamic Thermomechanical Analysis

Compared to the pure PEGDA based polymer, the elastic modulus for PP based composites at 25 $^{\circ}\text{C}$ increased slightly at low pollen loadings and then decreased continuously with increased pollen loading, while the loss modulus for composites at 25 $^{\circ}\text{C}$ remained stable generally (see Figure 5). For PEGDA-PP@5%, the G' value of the composite (3.4 MPa) was higher than that of the pure PEGDA polymer (3.1 MPa), which means that the addition of a small amount of pollen can enhance the mechanical properties of the composites. When more pollens were added, the G' value of PEGDA-PP@20% (0.21 MPa) was much lower than that of the pure PEGDA polymer. The change of G' value may be partly related to the presence of the voids in the composite and the shear dissipation by the pollen as fillers. From SEM, composites with pollen that display decreasing modulus

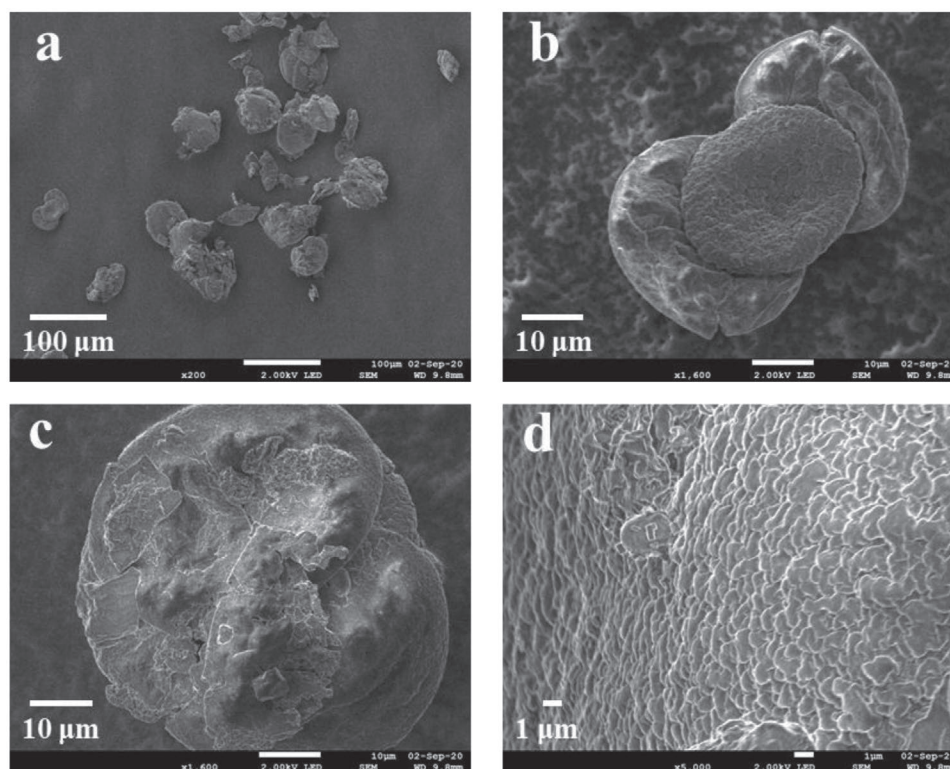


Figure 2. SEM images for pure pine-pollen, different views on different scales: a) 100 microns, b) 10 microns, c) 10 microns, d) 1 micron.

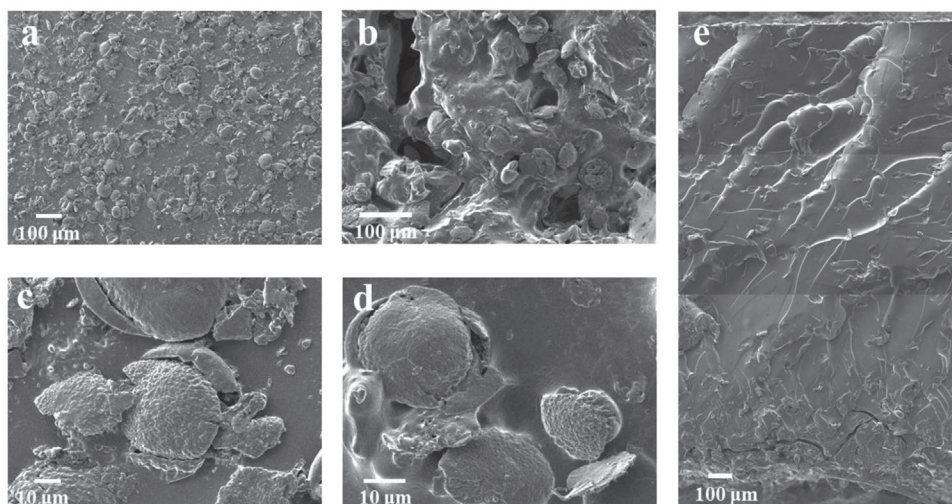


Figure 3. SEM images for PEGDA-PP@5%. a,c) irradiated face (top face), b,d) bottom face, e) cross section.

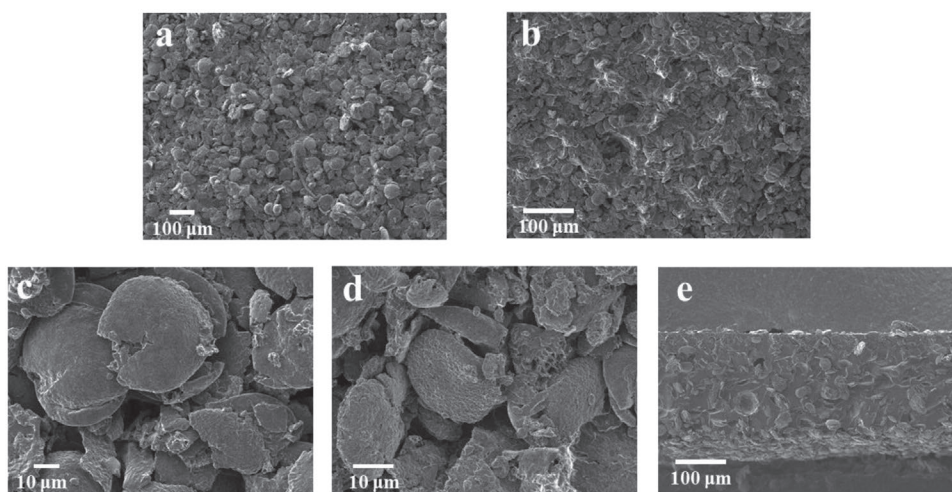


Figure 4. SEM images for PEGDA-PP@20%. a,c) irradiated face (top face), b,d) bottom face, e) cross section.

contain indeed more obvious interfacial voids after preparation. Therefore, with increasing pollen loading, the composite was increasingly softened as observed in other pollen based composites prepared by other polymerization techniques^[18] and the stiffness of these composites was effectively reduced.

3.4. Thermal Properties

In order to quantitatively illustrate whether the presence of PP can enhance the thermal stability of composites, TGA was carried out (Figure 6). As reported by Figure 6a, PP is characterized by weight loss between 50 and 500 °C which occurs in two steps. It is mainly associated with water desorption (50 to 200 °C) and then carbonization (200 to 500 °C).

In composites, a second weight loss appears between 350 and 500 °C (Figure 6a) and corresponds to the decomposition and carbonization of PEGDA based polymer. The temperature of the maximum decomposition rate T_{max} (Figure 6b, inflection point) is not significantly altered by the amount of PP (Table 1).

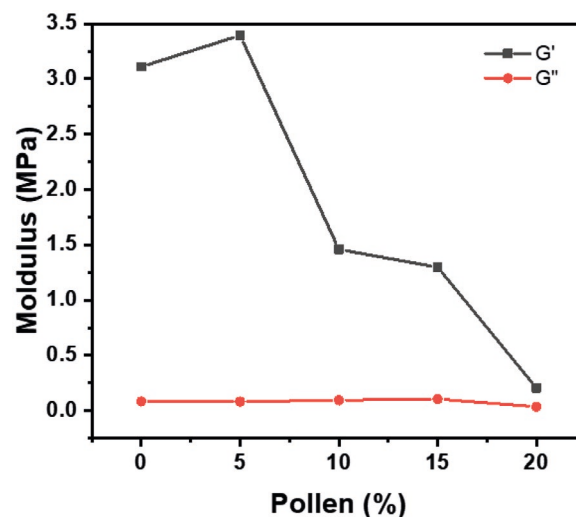


Figure 5. Dynamic thermomechanical analysis for composites with different pollen contents.

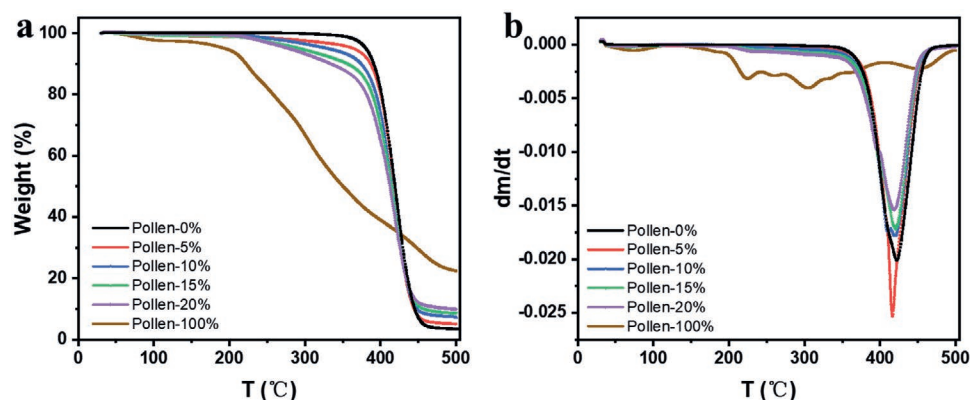


Figure 6. a) TGA and b) DTG for composites with different contents of pine pollen (wt%); monomer: PEGDA; photoinitiator: BDMK; polymerization @405 nm.

This result indicates that the pollen addition does not significantly affect the thermal stability of the polymer matrix.

3.5. Direct Laser Write of 3D Patterns

The significantly different effects of the PP content on the photopolymerization process of PEGDA have also been reflected in the DLW results. The DLW experiments were performed at 405 nm from the photocomposites with different pollen contents to generate the desired 3D patterns. Even when the filler content was 40%, 3D patterns also could be obtained through DLW process (see **Figure 7g**). As shown in **Figure 7**, the high reactivity of PP based resins allowed a very efficient photocuring process in the irradiated area, obtaining thick patterns with up to ≈ 1 mm thickness and excellent spatial resolution (within the size of the laser beam: ≈ 50 μ m) and in a short printing time (< 1 min for a 2 cm length 3D patterns). It is very clear from NOM images that as more pollens were used, the amount of pollen grains on the surfaces of patterns increased significantly. As the 3D color patterns morphology shown in **Figure 7b,d,f,h**, it can be observed that these 3D patterns remain very well resolved and their surfaces are flat between 5% and 20% of PP.

3.6. Water Swelling Property

In order to quantitatively illustrate the water swelling property of the PEGDA-PP composite with different PP contents, the water swelling experiments were carried out. As shown in **Figure 8**, the water swelling ratio was presented and its values decreased with the increasing pollen contents. Expressed in weight percentage, they decreased from 86.1 to 35.3 wt%, when the pollen content increased from 0% to 20%. Compared to

pure PEGDA polymer, these composites had a lower swelling compared to pure PEGDA polymers, which might be because the presence of pollen particles had an influence on the cross-linking of PEGDA in composites.

As shown in **Figure 9**, the pictures of the 3D patterns composites with different pollen contents before and after water sorption and after heating @50 °C for 1 h are reported. Characterization of composites by numerical optical microscopy are depicted in **Figure S5**, Supporting Information. It is easy to observe that the 3D patterns (e.g., the letter “L”) expanded after water absorbing and returned close to their origin shape after heating (water removal). In this hydration/heating cycle, the volumes were defined as follow: Volume before swelling (V_1), volume for the 1st water swelling (V_2), and volume after water removal (V_3) (**Table S2**, Supporting Information). Therefore, the tendency for the swelling ratio expressed as a volume percentage extracted from 3D patterns is presented in **Figure 8b**. It decreased from 190.2 to 68.7 vol%. Therefore, when more pollen was added, less water was absorbed. Interestingly, a decrease of the 3D patterns volume after heating could be observed after the first hydration/heating cycle, that is, $V_1 > V_3$ (**Tables S2,S3**, Supporting Information). This volume decrease could be caused by the incomplete cross-linked reaction during the DLW process, and when the 3D patterns were put in water, the unreacted PEGDA monomers or small oligomers generated in the photopolymerization as well as parts of the pollen that were not enough cross-linked could be dissolved or dispersed into water (leaching). PEGDA-PP@20% was chosen to carry out the water swelling procedure in multicycle processes and the data are listed in the **Table S3**, Supporting Information. The volume value (V_3) after heating in the second swelling processes was similar with that (V_3) in the first swelling processes, which were both lower than the original volume (V_1). The decrease of the 3D patterns mass also had the similar trends. Therefore, after one cycle, the leaching is complete. As shown in **Figure S6**, Supporting Information, compared to the original 3D patterns, more pollen could be observed on the 3D pattern surface after water swelling and heating processes, and the surface was also rougher than that of the original 3D patterns. This is also consistent with the hypothesis of leaching. In addition, after

Table 1. $T_{\max}$ highlighted by TGA for pollen, PEGDA, and composite materials.

Pollen [wt%]	0	5	10	15	20
$T_{\max}$ [°C]	422	416	420	420	419

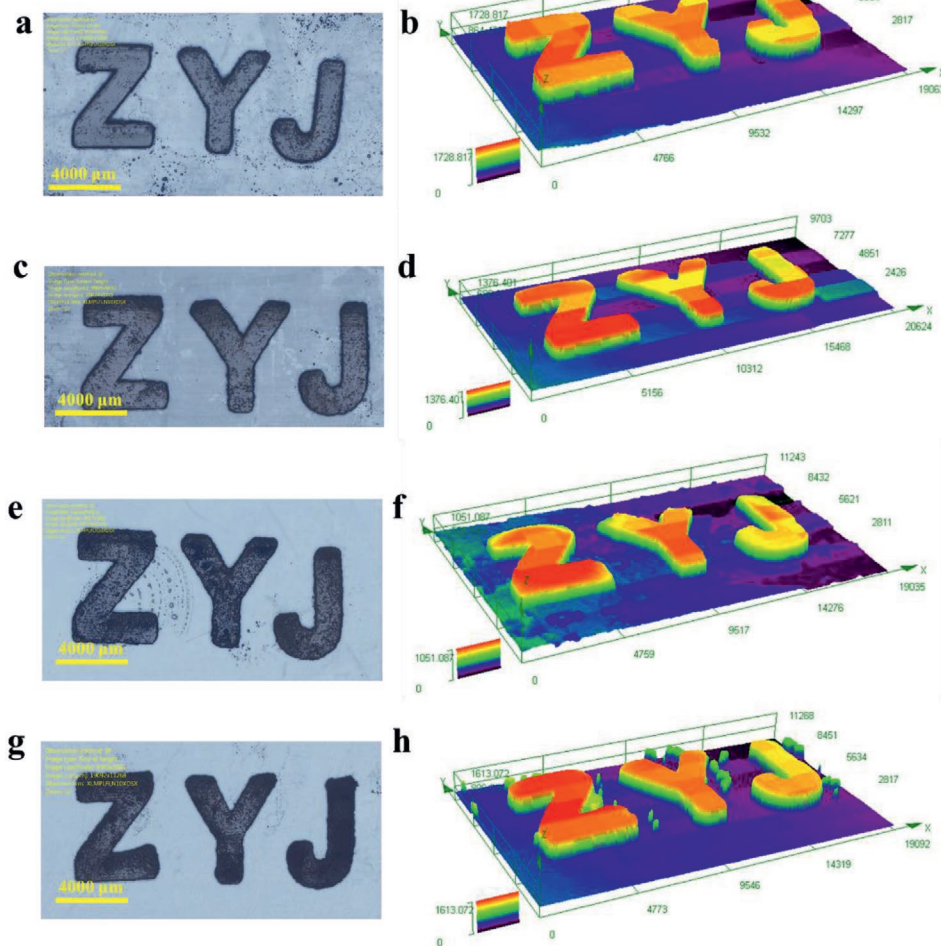


Figure 7. Free radical photopolymerization experiments for direct laser write experiments at 405 nm from a) PEGDA-PP@5%, c) PEGDA-PP@10%, e) PEGDA-PP@15%, g) PEGDA-PP@20% with 0.05 wt% BDMK and characterized by a numerical optical microscopy (NOM): Top surface morphology (a,c,e,g), color patterns (b,d,f,h). The photosensitive resins were spread in the tank. For all the samples, all the thickness was polymerized.

the water absorption and heating process, the size of pollen is basically unaffected.

However, compared to other composites, some cracks appeared during the heating on the surface of PEGDA-PP@5%

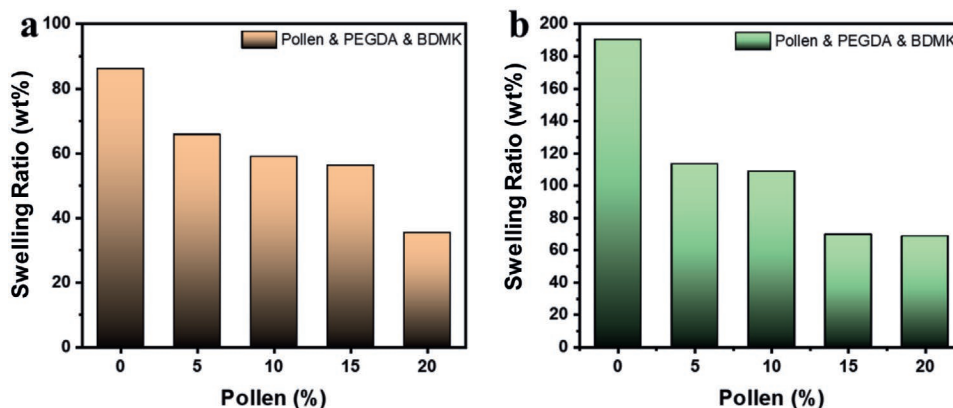


Figure 8. Swelling ratio of the composites with different filler contents. a) Swelling ratio with mass; b) swelling ratio with volume.

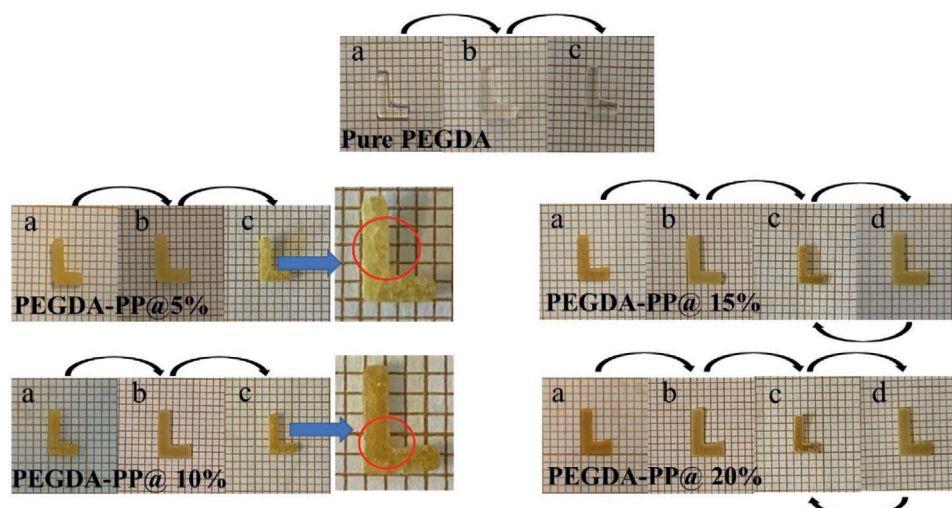


Figure 9. Photos of composites containing PP in water swelling experiments, contents of fillers: 5%, 10%, 15%, and 20%. The swelling process consists of 4 steps: a) Before water swelling, b) after water swelling, c) after water removal, and d) after water swelling again. (Monomer: PEGDA; photoinitiator: BDMK; polymerization @405 nm). Each small square in the background of each photo is the standard 1 mm × 1 mm size.

and PEGDA-PP@10% composites due to the presence of pollen and the high water-absorption of the composite with low pollen contents (see Figure 9 and Figure S5c, Supporting Information). Interestingly, when pollen contents were 15% and 20%, the processes of water absorbing and water removal could be accomplished many times. This meant that the 3D patterns with high pollen contents obtained through DWL can achieve repeated regular deformation under the influence

of the presence of water. This better resistance to hydration/heating processes and the associated changes of volume is in agreement with the softer character for high pollen contents associated with a decrease of the stiffness (better resistance to break). The plausible explanation is a decrease of the polymer network density in presence of PP leading to a softer material (more flexible) and therefore a shape memory effect (see below).

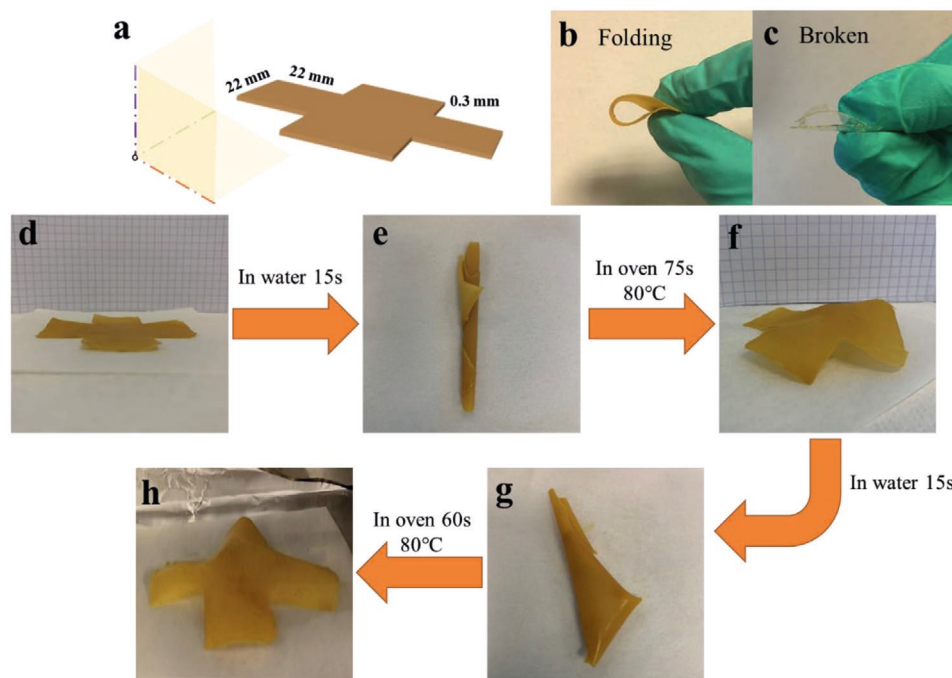


Figure 10. 4D printing process with water swelling and dehydration. a) Designed geometrical properties of cross; b) folding effect of composite; c) folding effect of pure PEGDA polymer (broken); d) top view of cross geometry (before water swelling); e) top view of cross geometry (after water swelling); f) top view of cross geometry (after water removal); g) top view of cross geometry (after water swelling again); h) top view of cross geometry (after water removal again).

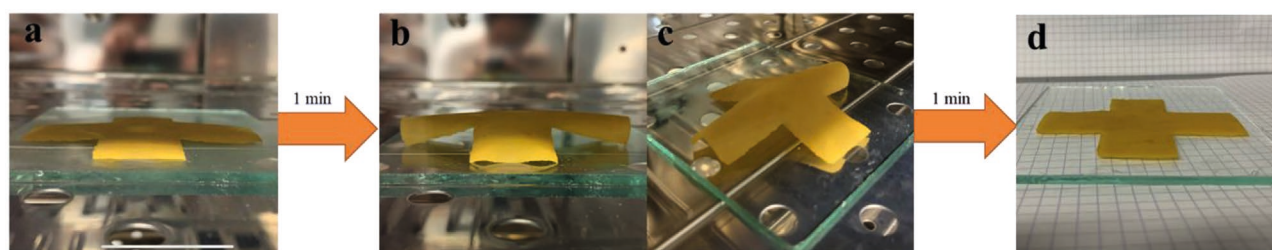


Figure 11. 4D printing process in the environment of humid air. a) view of cross geometry (before shape change); b,c) top view of cross geometry (after shape change); d) top view of cross geometry (put in general atmospheric environment (23 °C, 58.9 rh%)).

4. 4D Printing Application with PEGDA-PP@20%

Spatially control of 3D printed composites by photopolymerization, and even for 4D printing via swelling and dehydration induced actuation have been previously explored by several groups.^[30–32] Here, 4D printing products were manufactured through the water swelling and dehydration induced actuation of the 3D printed composites (PEGDA-PP@20%) with spatial resolution characteristics. A cross shaped object with spatially resolved properties was designed as shown in **Figure 10a**. After the manufacture with light irradiation at 405 nm for 30 s, this thin composite product has a good flexibility as shown in **Figure 10b**, in contrast the pure PEGDA polymer was broken as shown in **Figure 10c**. This shows that the better flexibility and resistance to stress for PP filled composites. This is because the presence of a large amount of pollen reduced the stiffness of the composite. Thus, the composite was softer than the pure PEGDA polymer.

In **Figure 10d,e**, the cross was taken into a water filled beaker and then we observed that it began to deform as the water swollen, which caused the cross curled completely after swelling in water for 15 s. Subsequently, the cross was removed from water and heated at 80 °C to induce evaporation. Correspondingly, as the contained water be removed, the curled cross would stretch again (see **Figure 10f**). As shown in **Figure 10g,h** the repeat operations, water swollen and water removal, could be implemented again. All these results demonstrated that the composites containing PP have a reversible deformation effect due to their thermo-responsive and water-responsive characters. The whole process for 4D printing is shown in Video S1, Supporting Information. Remarkably such a behavior is not possible for pure PEGDA polymers (see **Figure 10c**) showing the unique role of PP fillers in these thermo and water activations.

Based on this reversible deformation effect, the shape change was also obtained when the cross shaped object of PEGDA-PP@20% was put in the environment of humid air (30 °C, 80 rh%). In **Figure 11a**, the initial cross geometry is depicted. Then, the cross geometry had a very obvious shape change (the central part of the object was raised) after this cross geometry was exposed in the environment (30 °C, 80 rh%) for 1 min (**Figure 11b,c**). The cross geometry can rapidly revert to its original shape when this object was put in room environment (23 °C, 58.9 rh%) for 1 min without any heating process (**Figure 11d**). The interesting process can be repeated for many times. The whole process for 4D printing is shown in Video S2, Supporting Information.

5. Conclusion

In this work, we have successfully prepared photocomposites containing PP in the presence of BDMK at 405 nm LED irradiation under mild conditions. All these results demonstrated that PP leads to softer materials with reduced stiffness for better resistance to break compared to pure PEGDA based polymers. These mechanical properties can also be modulated with the PP content. Remarkably, PP/PEGDA photosensitive resins have a good spatial resolution in 3D printing and excellent behavior in swelling experiments. 4D printing were also manufactured through the water swelling and dehydration induced actuation of the 3D printed composites with spatial resolution features. Therefore, PP provided a valuable platform to study biosourced natural materials applied in the field of photopolymerization. This work would not only expand our understanding about the effect of fillers on the photopolymerization but also find important potential applications of photopolymerization reactions in the field of 3D printing, 4D printing, and microlithography.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

biosourced fillers, composites, photopolymerization, photopolymers

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